Novel calix[4]arenes bearing azinyl fragments at the meso-position have been synthesized through the direct, non-catalyzed by transition metals, cross-coupling reaction of π-deficient azaaromatic compounds with the lithium salts of tetramethoxycalixarenes. The approach is based on using the methodology of nucleophilic substitution of hydrogen (S_N^H) in heteroaromatic systems.

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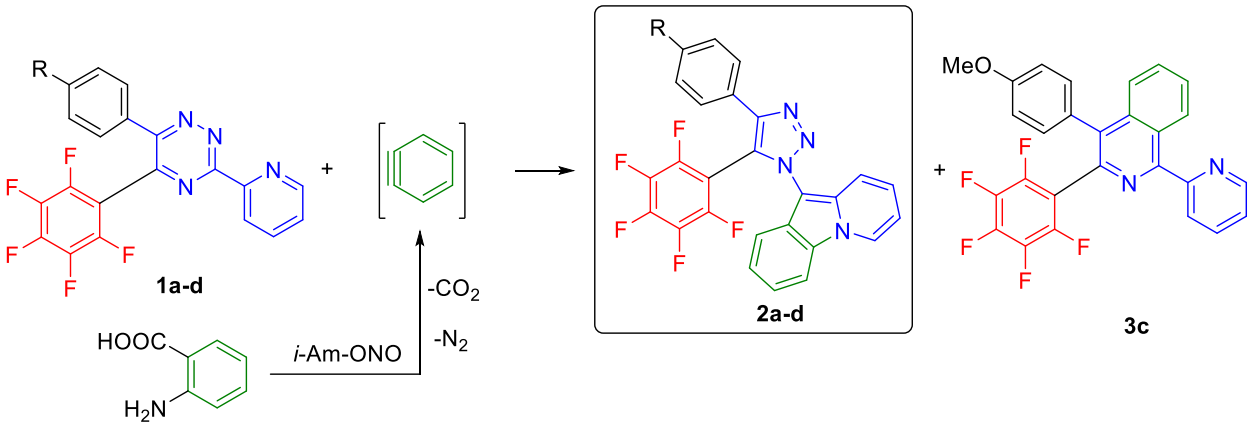
T. D. Moseev[1], M. V. Varaksin[1, 2], E. A. Nikiforov[1], A. P. Krinochkin[1, 2], D. S. Kopchuk[1, 2], G. V. Zyryanov[1, 2], O. N. Chupakhin[1, 2]★, V. N. Charushin[1, 2]

[1]Ural Federal University,
620002, Russia, Ekaterinburg, Mira St., 19,
[2]Institute of Organic Synthesis,
Ural Branch of the Russian Academy of Sciences,
620041, Russia, Ekaterinburg, S. Kovalevskaya St., 22,
chupakhin@ios.uran.ru

ARYNE-MEDIATED TRANSFORMATIONS OF 5-PERFLUOROPHENYL-SUBSTITUTED 3-(PYRIDIN-2-YL)-1,2,4-TRIAZINES*

Keywords: pyrido[1,2-*a*]indoles, aryne, rearrangement.

Fluorinated organic compounds are known to have many applications in various fields of science and technology. In particular, they can be regarded as fascinating candidates for medicinal and agricultural chemistry, as well as active ingredients in the design of new functional and photoactive materials for molecular electronics.



R = H (**a**), Me (**b**), OMe (**c**), Br (**d**)

Scheme 1. Aryne-mediated transformations of 5-(perfluorophenyl)-3-(pyridin-2-yl)-1,2,4-triazines **1(a-d)** in the synthesis of polyfluorinated 10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indoles **2(a-d)**

The starting materials for the synthesis of previously unknown 10-(4-aryl-1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indoles **2(a-d)** bearing pentafluorophenyl fragment at the C(5) position of triazole ring are 6-aryl-5-(perfluorophenyl)-3-(pyridin-2-yl)-1,2,4-triazines **1(a-d)**. These compounds were obtained according to the method [1], based on the reactions of nucleophilic substitution of hydrogen (S_N^H) in 3,6-disubstituted 1,2,4-triazines by action of pentafluorophenyllithium generated *in situ* from commercially available pentafluorobenzene.

Further interaction of 5-perfluorophenyl-1,2,4-triazines **1a-d** with 1,2-dehydrobenzene was carried out according to reported procedures [2] that had previously been used for the perfluorophenyl-free (pyridin-2-yl)-1,2,4-triazine substrates (Scheme 1). In order to generate aryne, diazotization of anthranilic acid was used. Finally, the products of the (pyridin-2-yl)-1,2,4-triazine system rearrangement, 10-(4-pentafluorophenyl-1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indoles **2(a-d)** containing pentafluorophenyl moiety at the C(4) position, were obtained in 51-54% yields. An exception was found in case of the interaction with triazine **1c** bearing *p*-methoxyphenyl at the C(6) position of azine ring. Herein, along with the 10-(4-(4-methoxyphenyl)-5-(perfluorophenyl)-1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indole **2c**, the classical aza-Diels-Alder reaction product, *i.e.* 4-(4-methoxyphenyl)-3-(perfluorophenyl)-1-(pyridin-2-yl)isoquinoline **3c**, was isolated in 7% yield. Thus, the incorporation of electron-withdrawing pentafluorophenyl moiety, was observed to lead to the classical aza-Diels-Alder reaction to be realized. It should be noted that, similar effects were observed earlier for other electron-withdrawing substituents, in particular for cyano group, phenylethynyl or styryl moieties, and the degree of the occurrence of the classical aza-Diels-Alder reaction was found to increase upon increasing the acceptor strength [3].

In summary, a number of novel polyfluorinated 10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indole green-emitting fluorophores have first been synthesized using combine strategy including S_N^H reactions in 3-(pyridin-2-yl)-1,2,4-triazines followed by aryne-mediated domino transformations of 5-(perfluorophenyl)-3-(pyridin-2-yl)-1,2,4-triazines.

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T. D. Moseev[1], M. V. Varaksin[1, 2], E. A. Virlova[1], O. N. Chupakhin[1, 2★], V. N. Charushin[1, 2]

[1]Ural Federal University,
620002, Russia, Ekaterinburg, Mira St., 19,
[2]Institute of Organic Synthesis,
Ural Branch of the Russian Academy of Sciences,
620041, Russia, Ekaterinburg, S. Kovalevskaya St., 22,
chupakhin@ios.uran.ru

DIRECT C-LI/C-H COUPLING OF C6F5LI WITH AZINES AND AZOLES N-OXIDES AS EFFICIENT APPROACH TOWARD TO POLYFLOORINATED AZAHETEROCYCLES*

Keywords: C-C coupling, nucleophilic substitution of hydrogen, fluorine, fluorarenes.

Polyfluorinated arenes, possessing a special structural organization and unique physicochemical properties, are one of the most common scaffolds in various biologically active molecules, agrochemicals, materials and substances for molecular electronics. It is known that the introduction of fluorine atoms or fluorinated building blocks increases the oxidative stability of organic molecules and, thus, prevents unwanted degradation transformations.